DETECTION OF THE C_4H RADICAL TOWARD IRC +10216

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ABSTRACT

Four emission doublets in the millimeter-wave spectrum of IRC +10216 have been identified as the $N = 9 \rightarrow 8$, $10 \rightarrow 9$, $11 \rightarrow 10$, and $12 \rightarrow 11$ rotational transitions of the C_4H radical. The rotation and spin-doubling constants of C_4H derived from the astronomical data are $B_0 = 4758.48 \pm 0.10$ MHz and $|\gamma| = 38.7 \pm 1.0$ MHz. The lines of C_4H in IRC +10216 are about as strong as those of the similar radical C_3N, but because of its smaller dipole moment, C_4H may be more abundant than C_3N by a factor of 4, with a column density in the range 4×10^{14} to 3×10^{15} cm^{-2}.

Subject headings: interstellar: molecules — molecular processes

There is growing evidence that conjugated carbon chains, highly unstable in the terrestrial laboratory, are among the most abundant large molecules in space. The long cyano-polyacetylenes (cyanopolyynes) HC_5N, HC_7N, and HC_9N have recently been discovered (Avery *et al.* 1976; Kroto *et al.* 1978; Broten *et al.* 1978), and an even more reactive chain, the cyanoethynyl radical C_3N, has been tentatively identified in the molecular envelope of IRC +10216 (Guélin and Thaddeus 1977). Several of the cyano-polyacetylenes have been synthesized in small quantities, and their astronomical detection is based on laboratory microwave spectra; C_3N, in contrast, has never been observed in the laboratory, and its astronomical identification rests solely on theoretical predictions of its microwave spectrum (Wilson and Green 1977).

We have now identified in IRC +10216 a very similar carbon chain, the butadiynyl radical C_4H, again at frequencies very close to those predicted by molecular structure theory. C_4H, like C_3N, is expected to be a linear molecule, and the millimeter-wave spectra of the two are so similar that fairly precise calculations of the rotation constants are required to tell them apart. The identification of C_4H hence corroborates nicely the reasoning which led to the identification of C_3N. Certain identification of both still requires laboratory spectra, but their presence in IRC +10216 is now subject to little doubt.

Figure 1 shows eight emission lines in the millimeter-wave spectrum of IRC +10216 which we attribute to C_4H; all were obtained with the NRAO[1] 36 foot (11 m) telescope at a spectral resolution of 1 or 0.5 MHz, four by us, four by other observers. We observed the lower two doublets in 1976 October, in an attempt to confirm C_3N by finding the $N = 10 \rightarrow 9$ and $9 \rightarrow 8$ rotational transitions of C_4H. For several reasons we were reluctant to conclude that these were the spin doublets of C_4H

we were seeking. The chief difficulty was instrumental. The signal-to-noise ratio was marginal, and the data suffered from bad spectrometer channels and baseline ripple; a number of similar features appeared in the several thousand MHz covered by our search, some real, others probably spurious, so the reality of the doublets was problematical. A secondary reason was theoretical. From electron spin resonance (ESR) studies on C_4H trapped in frozen inert gas matrices (Dismuke, Graham, and Weltner 1975), and by analogy with C_3N, we expected doublets only about half as wide as those in Figure 1.

The recent publication by Liszt (1978) of the spectrum second from the top in Figure 1, obtained in 1977 March during a search for the S_2 molecule, provided the additional information that convinced us that our doublets were real. Liszt pointed out that one of these lines might be dimethyl ether and the other NCO, but concluded that a spin doublet of unknown origin was a better interpretation of his data. This doublet and our two are of comparable intensity, and all are split by the same amount, 39 MHz, suggesting a common origin. A remarkable additional symmetry indicates that this is almost certainly so: the doublet center frequencies are precise high harmonics of a common fundamental. As Guélin and Thaddeus (1977) have shown, equally split millimeter-wave doublets harmonically related in this way are almost certainly spin doublets in the rotational spectrum of a large linear radical.

Evidence for yet a fourth rotational transition of the same radical in IRC +10216 also exists. The doublet at the top of Figure 1 was observed by Scoville and Solomon (1978) in 1977 October; they offered no explanation for the low-frequency line, but identified the high-frequency one as vibrationally excited CO. The splitting of this doublet is again 39 MHz, and the center frequency is very nearly harmonically related to the doublets which we and Liszt observe at lower frequency, so there is little doubt that we are all observing the same molecule. Whether the intensity asymmetry in Scoville and Solomon's doublet results
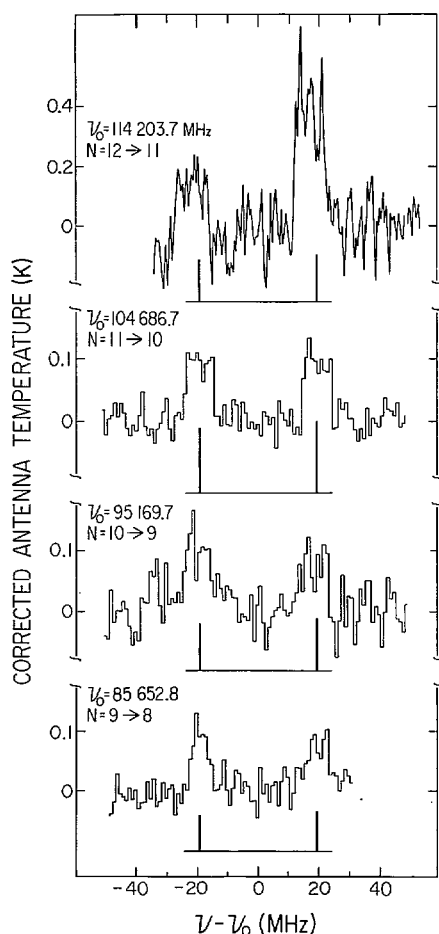
FIG. 1.—A comparison of lines in the millimeter-wave spectrum of IRC +10216 with a calculation of the rotational spectrum of C₄H (*vertical bars*). The doublet structure results from the interaction of the unpaired electron spin with the molecular rotation. The two lower doublets are new; the doublet second from the top was observed by Liszt (1978) but not identified; the doublet on top was observed by Scoville and Solomon (1978), who attributed the high-frequency component to vibrationally excited CO. The abscissa is rest frequency relative to the doublet center frequency ν_0, calculated on the assumption that the source velocity in the local standard of rest is −26 km s⁻¹, the velocity of cyanoacetylene in IRC +10216. The ordinate is antenna temperature corrected for atmospheric absorption.

from a blend with vibrationally excited CO, or is merely of instrumental origin, cannot be decided without further observation; because of the possibility of such a blend, however, we have excluded Scoville and Solomon's data from the analysis of the spectroscopic parameters of our new radical.

The theoretical spectra in Figure 1 have been calculated on the assumption that this radical is rigid, and possesses a $^2\Sigma$ electronic ground state. As a consequence, the frequency and intensity of the rotational spin doublets are a function of only two undetermined parameters, the rotation constant B_0 and the spin-doubling constant γ, which have been adjusted to give a best fit to our and Liszt's data. (Hyperfine structure can be neglected for the high rotational quantum numbers in question.) Intensities have been calculated on the assumption that all lines are optically thin, that the source is pointlike on the scale of the antenna beam (1′.1–1′.3) of the 36 foot telescope, and that the molecular rotational temperature is high enough ($\gtrsim 60$ K) so level populations are simply proportional to statistical weights. As Figure 1 shows, excluding Scoville and Solomon's doublet, 11 independent observational quantities—six line frequencies and five relative intensities—are accounted for to within the observational uncertainties by this two-parameter theoretical spectrum, so the presence of a large new linear radical in IRC +10216, whatever it may be, is hardly subject to doubt. A summary of the observational data, including a comparison of observed and calculated line frequencies, is given in Table 1.

That this new radical is C₄H is also fairly certain. We have surveyed enough of the spectrum of IRC +10216 between the doublets in Figure 1 to be reasonably sure that no intervening doublets exist, so those observed must be *successive* rotational transitions, with the quantum numbers given in Table 1 and Figure 1. The best-fit spectrum therefore yields a unique value for the rotation constant B_0, namely, one-half the common fundamental frequency. This empirical B_0 and the best-fit value of the spin-doubling constant γ are given in Table 2. For comparison, B_0 for C₄H computed by the Hartree-Fock method, and γ obtained from ESR on trapped C₄H, are also listed, as well as available data for C₃N.

TABLE 1

LINES IDENTIFIED AS C₄H IN IRC +10216

TRANSITION $N' \rightarrow N$	REST FREQUENCY (MHz)		LINE WIDTH (MHz)	INTENSITY $(T_A{}^*)$ (K)	REFERENCE
	Observed	Calculated			
12→11.....	114221	114223.0	10	0.40	Scoville and Solomon 1978
	114182	114184.3	11	0.23	
11→10.....	104706.0	104706.0	10	0.10	Liszt 1978
	104667.3	104667.3	9	0.10	
10→9......	95189.0±1	95189.0	9	0.08	This *Letter*
	95149.5±1	95150.3	8	0.08	
9→8.......	85672.4±1	85672.1	8	0.07	This *Letter*
	85633.9±1	85633.4	8	0.08	

TABLE 2

ROTATION AND SPIN-DOUBLING CONSTANTS OF C_3N AND C_4H

MOLECULE	B_0 (MHz)		γ (MHz)	
	Observed	Hartree-Fock	Observed	ESR
C_3N.......	4947.66 ± 0.10[a]	4955 ± 50[b]	$\pm 18.7 \pm 0.5$[a]	
C_4H.......	4758.48 ± 0.10	4753 ± 50[b]	$\pm 38.7 \pm 1.0$	18 ± 6[c]

[a] Guélin and Thaddeus 1977, plus recent observations of the $N = 11 \rightarrow 10$ transition. The new data yield $D_0 = 1 \pm 0.5$ kHz.

[b] Wilson and Green 1977.

[c] Dismuke, Graham, and Weltner 1975.

B_0 for our new molecule agrees to within about 0.1% with that calculated for C_4H, and it is this agreement between theory and observation which constitutes the basis of our identification of C_4H. No other molecule that we have considered, real or hypothetical, accounts satisfactorily for the observational data. Further astronomical tests are possible (hyperfine structure in the low rotational transitions, for example), but laboratory spectroscopy on C_4H is probably required to significantly improve our confidence in this assignment.

Centrifugal distortion of C_4H is not apparent in our and Liszt's data. A reasonable upper limit on the centrifugal distortion constant D_0 is about 1 kHz, which is consistent with the value for C_3N, 1 ± 0.5 kHz (Table 2). The center of Scoville and Solomon's doublet, however, is shifted about 2 MHz below the expected rigid rotor frequency. The fundamental rotational transition of first vibrationally excited CO lies by chance only 1.3 MHz below the predicted upper component of the $N = 12 \rightarrow 11$ C_4H transition; whether this 2 MHz shift results from a blend with vibrationally excited CO, centrifugal distortion, or a slight error in frequency measurement (or a combination of these) is unclear.

The theoretical spectrum in Figure 1 has been calculated with γ positive, with the result that the upper component in each doublet is predicted to be stronger than the lower by about 10%; for γ negative the lower component would be the stronger. The spectra are clearly not good enough to rule out this alternative, so from the astronomical data alone the sign of γ is unknown. It should be possible with better observations to resolve this ambiguity.

The discrepancy of over a factor of 2 between the spin-doubling constant which we determine for the free C_4H radical and that obtained from electron spin resonance on trapped C_4H does not appear to constitute an objection to our assignment. The spin-doubling constant cannot be directly measured by ESR; it is instead inferred from measurement of the components of the gyromagnetic ratio of the unpaired electron spin. This estimate is good for some molecules (notably the diatomic metal hydrides and fluorides) but poor for others. In particular, ESR underestimates γ by a factor of over 2 for CN, and a factor of 3 for C_2H—the radicals most similar to C_4H for which γ is known and ESR data exist (Turner and Gammon 1975; Tucker,

Kutner, and Thaddeus 1974; Knight and Weltner 1970). For C_4H, we therefore conclude that no serious discrepancy exists between the astronomical and ESR values of γ, and that the difference between the two is actually of the order expected. Although often unreliable as a measure of the magnitude of γ for a free radical, ESR on the trapped radical usually determines the sign correctly. The sign of γ for C_4H, undetermined by the astronomical data, is therefore probably positive.

Only a rough estimate of the amount of C_4H or C_3N in the molecular envelope of IRC +10216 is possible, since for each the rotational partition function is poorly known. Let us assume that rotational populations are approximately characterized by a rotational temperature T_{rot}, and that all observed millimeter-wave lines are optically thin. The millimeter-wave spectra imply that $T_{rot} \gtrsim 60$ K, and it would be surprising if T_{rot} were greater than 600 K, the infrared color temperature of IRC +10216 (Barnes et al. 1977). Assuming hence that $60 \lesssim T_{rot} \lesssim 600$ K, and adopting the *ab initio* theoretical values for the permanent electric dipole moments of C_4H and C_3N (0.9 and 2.2 debye, respectively, according to Wilson and Green 1977), the observational data imply the following column densities:

$$4 \times 10^{14} \lesssim N_{C_4H} \lesssim 3 \times 10^{15} \, \text{cm}^{-2},$$

and

$$1 \times 10^{14} \lesssim N_{C_3N} \lesssim 8 \times 10^{14} \, \text{cm}^{-2}.$$

Although the lines of C_4H and C_3N are comparably strong in IRC +10216, because of its smaller dipole moment, C_4H seems to be the more abundant by roughly a factor of 4.

In summary, four doublets in the millimeter-wave spectrum of IRC +10216 have been identified as successive rotational transitions of the linear C_4H radical. The observed rotation constant of C_4H agrees to within about one part per thousand with the rotation constant obtained from a Hartree-Fock calculation. Identification of C_4H considerably enhances the confidence that can now be placed in the previous identification of the similar radical C_3N. Detection of both of these reactive molecules in the laboratory, the best way to confirm the astronomical identifications, now poses a clear challenge to the microwave spectroscopist.

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